(54) Title: ADHESIVE COMPOSITIONS FOR BONDING PASSIVE SUBSTRATES SUCH AS MAGNESIUM ALLOYS

Dependence of lap-shear adhesive strength of room temperature curing time of Composition 5 with and without 0.25% ATPB; (magnesium substrates; "zero" gap)

Stress at break (MPa)

Room Temperature Curing Time (hours)

Base Composition 5 (mixture of urethane-acrylate monomers, hydroxypropyl methacrylate, acrylic acid, CHP, and 1-acetyl-2-phenylhydrazine)

Base Composition + 0.25% allytriphenylphosphonium bromide (ATPB)
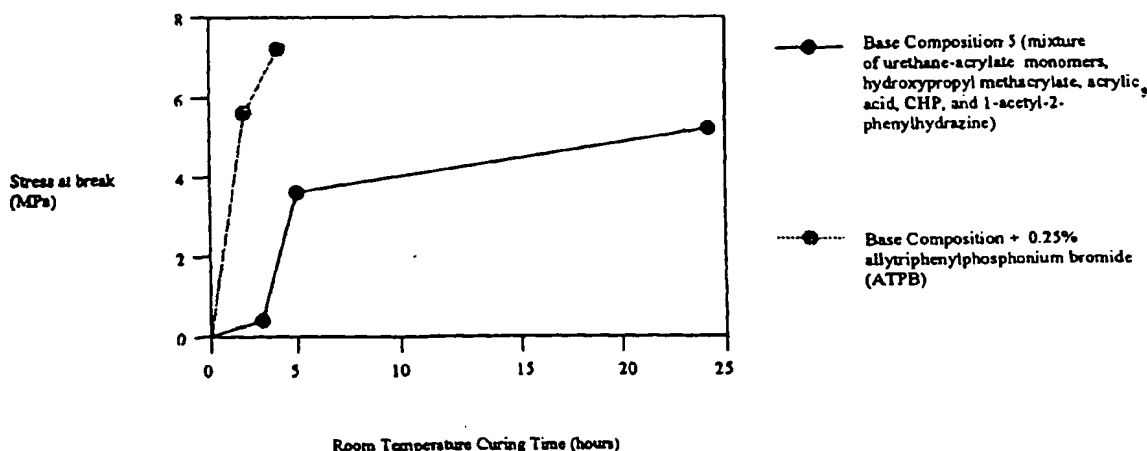
(57) Abstract: Adhesive compositions are disclosed which cure rapidly and completely on confinement between passive substrates, such as magnesium alloys, that are deficient in transition metals and transition metal ions. The compositions include one or more acrylate resins, one or more peroxy free radical initiators, one or more onium salts, and an accelerator such as acetylphenyl hydrazine desirably in an amount of about 1.0 % or less by weight of the composition. These compositions provide exceptional bonding to such substrates without the need for a transition metal primer. Methods of making and using such compositions are also disclosed.

ADHESIVE COMPOSITIONS FOR BONDING PASSIVE SUBSTRATES SUCH AS MAGNESIUM ALLOYS

FIELD OF THE INVENTION

The present invention relates generally to compositions for bonding magnesium-based substrates. More particularly, the present invention relates to compositions which demonstrate excellent bonding capabilities to magnesium-based and other passive

5   substrates without the need for the application of a primer prior to application of the composition on the substrate. These compositions are storage-stable and cure rapidly and thoroughly, particularly under anaerobic conditions.

BACKGROUND OF RELATED TECHNOLOGY

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Anaerobic compositions are stable and remain in a liquid, unpolymerized state in the presence of oxygen, but cure to a polymerized, solid state in the absence of oxygen. Such compositions are generally characterized as being one-part systems, with the ability to cure at room temperature through a free radical reaction, and to cure through a

15   reaction initiated on a substrate surface. The components of such compositions are often monomers, initiators, catalysts, stabilizers/inhibitors, and modifiers, which may be combined, typically by mixing, to provide formulations of various viscosities, colors, strengths, and adhesion properties.

As a result of their ability to cure in a substantially oxygen-free environment, anaerobic compositions have found great utility as adhesives, sealants, and bonding materials for use with closely mated surfaces, such as between interfitting metal parts. Known industrial uses include locking threaded fasteners, sealing threaded pipe

5   connections, retaining cylindrical machine components, sealing flange joints, bonding structural components, and sealing porous metal castings. Anaerobic adhesives are typically packaged, sold and stored in containers which are permeable to oxygen, such as those made of polyethylene.

10   Cure of anaerobic compositions is usually accelerated by the presence of a suitable metal, such as a transition metal (e.g., iron, copper, and nickel), which renders such metals well-suited for bonding with such compositions. However, such metals are susceptible to corrosion, often times rendering them poorly suited for industrial applications where corrosion compromises the integrity of the parts.

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In contrast, magnesium alloys, typically alloys which include magnesium, aluminum, zinc and manganese, are passive substrates which are characterized as having high resistance to corrosion and a high strength-to-weight ratio. Additionally, they are easily molded and have the ability to withstand high tolerances and high temperatures.

20   As a result of these properties, magnesium alloys are finding utility in many commercial applications, such as automotive applications.

Magnesium alloys have traditionally been joined by riveting or welding. It is desirable, however, to bond magnesium alloys using adhesives, as this offers advantages

25   in weight saving, fatigue strength, and corrosion resistance. Corrosion resistance is due

in large part to the very low level or iron, copper, and nickel found in most common

alloys. The lower quantity of these transition metals present in an alloy, the slower the

rate of corrosion. However, the low level of these transition metals renders magnesium

alloys particularly insensitive to anaerobic cure.

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Iron and copper have been found to accelerate cure of anaerobic adhesives and

typical anaerobic formulations generally require trace amounts of these elements to be

present to effect cure. These elements are generally applied to the substrate surface as a

primer prior to application of the anaerobic adhesive. Adhesive systems using such

10   primers are known as two-part systems.

United States Patent No. 5,411,998 to McArdle et al. discloses the use of

anaerobic compositions in one and two part systems for sealing surfaces having thick

bondlines. The one-part systems include as a cure system the combination of saccharin

15   and an onium salt. Example 18 of McArdle also discloses a two-part system, with each

part having a cure system, the first part including cumene hydroperoxide, saccharin and

an onium salt, and a second part which includes saccharin and acetylphenyl hydrazine.

Cure is achieved when the two parts are mixed together in equal amounts.

20   The additional step of treating the surface of the substrate with a primer is

undesirable as compared with one-part systems not requiring a primer as the need for a

primer renders the adhesive more expensive, more labor intensive to apply, and more

difficult to package and distribute. Therefore, there exists a need for a method of

bonding magnesium alloy substrates and related passive substrates using one-part

anaerobic adhesive systems. The present invention provides a solution to meet this

need.

SUMMARY OF THE INVENTION

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The present invention is directed to compositions which are suitable for use as

sealants, bonding agents, and threadlocking agents for magnesium-based and related

passive substrates. More particularly, the present invention is directed to a one-part

anaerobic adhesive for use in connection with bonding magnesium alloys and related

10   passive substrates. The compositions contain one or more monomers, one or more

peroxide initiators, one or more onium salts, and an organic hydrazine. Desirably the

organic hydrazine is present in an amount of about 1.0% or less by weight of the

composition. The compositions may optionally include saccharin, phenolic stabilizers,

chelating agents, and various additives for modifying the uncured and cured bonding

15   properties of the composition. The resulting activated adhesives cure rapidly and

thoroughly on confinement between magnesium alloys and other passive substrates.

In one desired aspect of the present invention is provided an adhesive

composition having improved bonding to passive substrates such as magnesium. The

20   composition includes at least one monomer, at least one peroxy free radical initiator, at

least one onium salt, and at least one organic hydrazine. Desirably, the organic

hydrazine is present in an amount of up to about 1.5 % by weight of the composition.

The monomer may be anaerobically curable or may be curable by a moisture cure

mechanism, heat cure mechanism, photo initiator mechanism, or a combination thereof.

25   The monomer may be a (meth)acrylate monomer, such as a polyurethane (meth)acrylate

monomer, the peroxy free radical initiator may be cumene hydroperoxide, and the onium

salt may be a phosphonium salt, an ammonium salts or a combination thereof. The

phosphonium salt may be present in an amount from about 0.25 to about 2.0 % by

weight of the composition. The composition may additionally include saccharin,

5   dimethyl p-toluidine, phenolic stabilizers, chelating agents, and combinations thereof.

        In a method aspect of the present invention is provided a method for providing

enhanced bonding to passive substrates such as magnesium which includes the steps of:

(a) providing a composition which includes at least one monomer, at least one peroxy

10   free radical initiator, at least one onium salt, and at least one organic hydrazine; (b)

disposing the composition between two substrates; and (c) effecting cure of the

composition to effectuate enhanced bonding thereof.

        In another method aspect of the present invention is provided a method of making

15   an anaerobic adhesive composition having improved bonding to passive substrates such

as magnesium which includes the steps of: (a) providing at least one monomer, at least

one peroxy free radical initiator, at least one onium salt; and at least one organic

hydrazine; and (b) combining each of the components to form a mixture.

20   **BRIEF DESCRIPTION OF THE DRAWINGS**

        Figure 1, 2 and 3 are graphs showing lap-shear test results on magnesium

substrates at zero gap and .254 mm gap for anaerobic compositions with and without the

addition of various concentrations of a phosphonium salt.

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Figure 4 is a graph showing an infrared spectroscopic plot of the fractional cure conversion as a function of cure time of anaerobic adhesives of the present invention as compared to the same composition without the onium salt.

5   Figure 5 is a graph showing the rate of cure on magnesium of the inventive composition as compared to the same composition without the onium salt.

DETAILED DESCRIPTION OF THE INVENTION

10   The present invention relates to adhesive compositions which are capable of sealing, bonding, and threadlocking magnesium-based and related passive substrates. Desirably, the present invention relates to one-part anaerobic adhesives. Known anaerobic adhesives used to seal and bond passive substrates require the use of a primer containing a transition metal that serves to catalyze polymerization of the monomer

15   which is present. Thus, conventional anaerobic compositions for passive substrates are two-part bonding systems. Additionally, known anaerobic compositions, such as those disclosed in the '998 patent, require the use of peroxide and saccharin in combination with an onium salt in order to effect desired curing. The '998 patent also discloses a two part adhesive system where the first part includes saccharin, peroxide and an onium salt

20   as the cure system, and the second part includes saccharin and acetylphenyl hydrazine as a second cure system. By contrast, it has been found that the present invention permits rapid and full cure of one-part anaerobic compositions on passive substrates without the need for a primer, without the need for saccharin, and by inclusion of a hydrazine compound. Accordingly, the present invention provides an economical and efficient

25   adhesive compound for bonding magnesium-based and related passive substrates.

The one-part anaerobic compositions of the present invention exhibit accelerated

cure and improved bonding as a result of the addition of onium salts, particularly

phosphonium salts, and an organic hydrazine which is present in an amount of less than

1.0% by weight of the composition. For example, these compositions desirably contain

5   mixtures of methacrylate ester resins, monomers and crosslinkers (desirably 50-98% by

weight), peroxides or hydroperoxides (desirably 0.1-10%), one or more onium salts, and

an organic hydrazine such as acetyl phenylhydrazine (APH), which is desirably present

in an amount of about 1.0% or less by weight of the composition. The compositions may

optionally contain other components including saccharin, dimethyl p-toluidine (DMPT),

10   phenolic stabilizers, chelating agents, and various additives for modifying properties of

the uncured and cured compositions.

Compositions of the present invention cure rapidly and completely on

confinement between magnesium alloys and related passive substrates that are deficient

15   in transition metals and transition metal ions such as iron, copper, and nickel. In

contrast, conventional anaerobic adhesives exhibit slow and incomplete curing on such

substrates. The adhesives of the present invention are desirably stable one-part products

under ambient storage conditions, but polymerize rapidly in contact with magnesium and

magnesium alloys. Alternatively, the adhesives of the present invention may be used in

20   conjunction with a primer. Surface primers are not required to induce curing, but may be

used to further enhance curing rates or to promote even further adhesion to the

substrates.

The adhesives of the present invention are tolerant of a wide variety of traditional

25   anaerobic adhesive curing agents and additives including ortho-Benzoic Sulfimide,

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DMPT, chelators and stabilizers, which permit existing products to be easily modified for use on magnesium surfaces. In addition, such additives may enhance the reactivity and other properties of the adhesives.

5   Any suitable monomer may be used in the adhesives of the present invention. Desirably, the monomers used in the present invention are (meth)acrylate monomers. Such monomers are desirably characterized as being either flexible or rigid. It will be apparent to one of ordinary skill in the art that the choice of monomers is dependent on the desired properties of the resultant curable product. Within the (meth)acrylate

10   component are a wide variety of mono(meth)acrylate materials represented by $H_2C=CGCO_2R^{15}$, where G may be hydrogen, halogen or alkyl of 1 to about 4 carbon atoms, and R^{15} may be selected from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl or aryl groups of 1 to about 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with such substituents as silane, silicon,

15   oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, carbamate, amine, amide, sulfur, sulfonate, sulfone and combinations thereof.

           Additional anaerobic curing monomers useful in the present invention include the alkylene glycol diacrylates having the general formula:

20

$$H_2C=\overset{\displaystyle}{\underset{\displaystyle R^4}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O-\left[(CH_2)_m-\left(\overset{\displaystyle R^6}{\underset{\displaystyle R^5}{C}}-\overset{\displaystyle R^6}{\underset{\displaystyle R^6}{C}}-O\right)_p\right]_n-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle R^4}{C}=CH_2$$
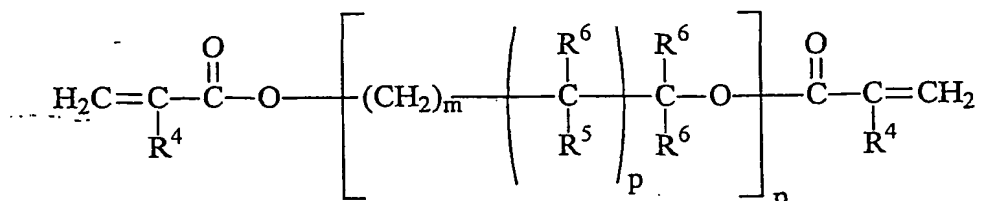
where R^6 represents a radical selected from the group consisting of hydrogen, lower

alkyl of 1- 4 carbon atoms, inclusive, hydroxyalkyl of 1-4 carbon atoms inclusive, and

$$-CH_2-O-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle R^4}{C}=CH_2$$
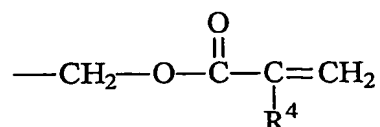
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wherein R^4 is a radical selected from the group consisting of hydrogen, halogen, and

lower alkyl of 1-4 carbon atoms; R^5 is a radical selected from the group consisting of

hydrogen, -OH and

$$-O-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle R^4}{C}=CH_2$$
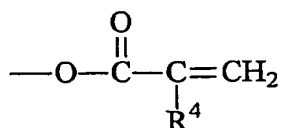
10   m is an integer equal to at least 1, desirably 1-8 and more desirably from 1 to 4; n is an

integer equal to at least 1, desirably 1 to 20; and p is 0 or 1.

    Typical of these monomers are mono-, di-, tri- tetra- and polyethylene glycol

dimethacrylate and the corresponding diacrylates; di(pentamethylene glycol)

15   dimethacrylate; tetraethylene glycol di(chloroacrylate); diglycerol diacrylate; diglycerol

tetramethacrylate; butylene glycol dimethacrylate; neopentyl glycol diacrylate; and

trimethylopropane triacrylate.

Useful polymerizable crosslinkable components are ethoxylated

trimethylolpropane triacrylate, trimethylol propane trimethacrylate, dipentaerythritol

monohydroxypentacrylate, pentaerythritol triacrylate, ethoxylated trimethylolpropane

triacrylate, 1,6-hexanedioldiacrylate, neopentyl glycoldiacrylate, pentaerythritol

5   tetraacrylate, 1,2-butylene glycoldiacrylate, trimethylopropane ethoxylate

tri(meth)acrylate, glyceryl propoxylate tri(meth)acrylate, trimethylolpropane

tri(meth)acrylate, dipentaerythritol monohydroxy penta(meth)acrylate, tri(propylene

glycol) di(meth)acrylate, neopentylglycol propoxylate di(meth)acrylate, 1,4-butanediol

di(meth)acrylate, polyethyleneglycol di(meth)acrylate, triethyleneglycol

10   di(meth)acrylate, butylene glycol di(meth)acrylate, ethoxylated bisphenol A

di(meth)acrylate and combinations thereof.

Other useful monomers include those acrylates derived from bisphenol-A, such

as bisphenol-A dimethacrylate, hydrogenated bisphenol-A dimethacrylate, and

15   ethoxylated bisphenol-A di(meth)acrylate.

While di- and other polyacrylate esters have been found particularly desirable,

monofunctional acrylate esters (esters containing one acrylate group), which may

conform to the aforementioned monofunctional (meth)acrylate structure also may be

20   used. When dealing with monofunctional acrylate esters, it is desirable to use an ester

which has a relatively polar alcoholic moiety. Such materials are less volatile than low

molecular weight alkyl esters and, more importantly, the polar group tends to provide

intermolecular attraction during and after cure, thus producing more desirable cure

properties, as well as a more durable sealant or adhesive. Particularly desirable are the

25   polar groups selected from labile hydrogen, heterocyclic ring, hydroxy, amino, cyano,

and halogen polar groups. Useful examples of compounds within this category include

cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, hydroxyethyl acrylate,

hydroxypropyl methacrylate, t-butylaminoethyl methacrylate, cyanoethylacrylate, and

chloroethyl methacrylate. The materials are often incorporated as reactive diluents

5   which are capable of copolymerizing with the various other polymerizable materials.

More specific (meth)acrylate monomers particularly desirable for use herein

include polyethylene glycol di(meth)acrylates, desirably triethyleneglycol

di(meth)acrylate, hydroxypropyl (meth)acrylate, bisphenol-A di(meth)acrylates, such as

10   ethoxylated bisphenol-A (meth)acrylate ("EBIPA" OR "EBIPMA"), and tetrahydrofuran

(meth)acrylates and di(meth)acrylates, citronellyl acrylate and citronellyl methacrylate,

hexanediol di(meth)acrylate ("HDDA" or "HDDMA"), trimethylol propane

tri(meth)acrylate, tetrahydrodicyclopentadienyl (meth)acrylate, ethoxylated trimethylol

propane triacrylate ("ETTA"), triethylene glycol diacrylate and triethylene glycol

15   dimethacrylate ("TRIEGMA").

For purposes of illustration only, listed herein are examples of urethane-acrylate

monomers suitable for use in the present invention. However, it is to be understood that

any acrylate resin, including non-urethane acrylates and methacrylates may be used in

20   the present invention. Desirably, monomers used is the present invention are

polyurethane polyacrylate monomers. Examples of such monomers are described in

United States Patent No. 3,425,988 to Gorman et al., specifically incorporated by

reference herein. These monomers may be represented by the following general

formula:
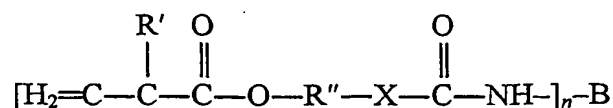
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$$[H_2{=}C{-}\overset{\displaystyle R'}{\overset{\displaystyle |}{C}}{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}{-}O{-}R''{-}X{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}{-}NH{-}]_n{-}B$$

5　　　wherein B is a polyvalent organic radical selected from the group consisting of alkyl,

alkenyl, cycloalkyl, aryl, aralkyl, alkaryl and heterocyclic radicals both substituted and

unsubstituted; X is selected from the group consisting of —O— and

$$\overset{\displaystyle R}{\overset{\displaystyle |}{-N-}}$$

10

radicals; n is an integer from 2 to 6 inclusive; R' is a member selected from the class

consisting of hydrogen, chlorine and methyl and ethyl radicals; and R'' is a divalent

organic radical selected from the group consisting of lower alkylene of 1 to 8 carbon

15　　　atoms, phenylene and naphthalene radicals.

Additional urethane-acrylate-capped poly(alkylene) ether polyol monomers, such

as those described in United States Patent No. 4,018,851 to Baccei, specifically

incorporated by reference herein, may be used in the present invention. Such monomers

20　　　may be represented by the following formula:

$$[CH_2{=}\overset{\displaystyle R^1}{\overset{\displaystyle |}{C}}{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}{-}O{-}R^2{*}I{*}D_d{*}I_i]_z Z$$
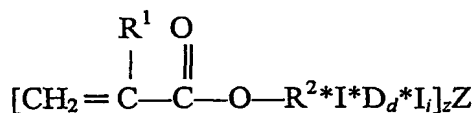
where R^1 is selected from the group consisting of hydrogen, chlorine and methyl and

ethyl radicals; R^2 is a divalent organic radical selected from the group consisting of

lower alkylene of 1-8 carbon atoms, phenylene and naphthalene; I is a polyisocyanate

radical; D is an aromatic, heterocyclic or cycloaliphatic polyol or polyamine radical,

5   desirably a diol, and more desirably a diol of a cycloaliphatic compound; Z is a

polymeric or copolymeric grafted alkylene ether polyol or alkylene ether polyol radical; z

is an integer corresponding to the valency of Z; d is either 1 or 0; and i is 0 when d is 0,

and otherwise equal to one less than the number of reactive hydrogen atoms of D. As

used herein, an asterisk (*) indicates a urethane ($-N-H-COO-$) or ureide

10   ($-NH-CO-NH-$) bond.

Further, urethane-acrylate-capped polybutadiene-based monomers, such as those

described in United States Patent no. 4,295,909, to Baccei, specifically incorporated by

reference herein, may be used in the present invention. Such polymers may be

15   represented generally by the following formula:

$$[CH_2 = \overset{\overset{\textstyle R''}{\textstyle |}}{C} - \overset{\overset{\textstyle O}{\textstyle \|}}{C} - O - R'''*I*D_d*I_i]_z Z$$
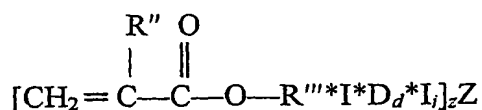
20   where R'' is selected from the group consisting of hydrogen, chlorine and methyl and

ethyl radicals; R''' is a divalent organic radical selected from the group consisting of

lower alkylene of 1-8 carbon atoms, phenylene and naphthalene; I is a polyisocyanate

radical; D is an aromatic, heterocyclic or cycloaliphatic polyol or polyamine radical,

desirably a diol of a cycloaliphatic compound; Z is a polymeric or copolymeric polyol or

25   poly radical of butadiene, the latter having a degree of polymerization of from about 5 to

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150 and at least about 70 percent of the polybutadiene portion of the 1,4-configuration; z is an integer corresponding to the valency of Z; d is either 1 or 0; and i is 0 when d is 0, and otherwise is equal to one less than the number of reactive hydrogen atoms of D. As used herein, an asterisk (*) indicates a urethane (—N—H—COO—) or ureide

5   (—NH—CO—NH—) bond.

While the present invention is particularly well suited to anaerobic compositions, it is in no way limited to compositions which cure under anaerobic conditions, nor is it limited to the use of (meth)acrylate-based monomers. For example, additional

10   monomers which are known to cure through free radical polymerization reactions could be used in the present invention. Examples of such monomers include, but are not limited to, styrene, thiol-enes, acrylamides, maleate esters, fumarates, methylene maleates, and epoxides. Further, the addition of various functional groups to (meth)acrylate monomers which may be used in the present invention will permit the

15   inventive compositions to cure in a variety of ways, such as by moisture, room temperature, heat and light. For instance, the addition of a photoinitiator to compositions of the present invention will permit dual curing (under anaerobic conditions and by light) of the compositions.

20   The present invention also includes a suitable initiator which will effect polymerization of the monomer. Desirably, such initiators are peroxy free radical initiators, such as those described in United States Patent No. 4,287,330 to Rich, specifically incorporated herein by reference. Desirably, the peroxy free radical initiator used in the present invention is an organic hydroperoxide such as cumene hydroperoxide

25   (CHP), methylethyl ketone hydroperoxide, or t-butyl hydroperoxide. Additional
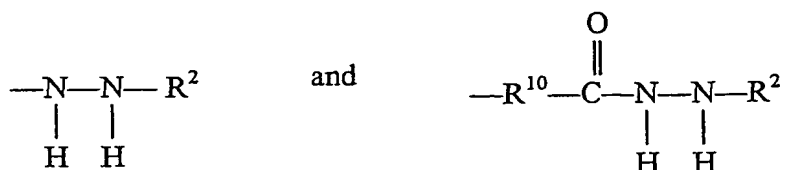
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hydroperoxides may also be used, such as *p*-menthane hydroperoxide,

diisopropylbenzene hydroperoxide, and pinene hydroperoxide. The initiator is desirably

present in an amount sufficient to initiate polymerization of the monomer. The initiators

set forth above are forth for the purposes of illustration only and are in no way meant to

5   limit the initiators that may be used in the present invention.

The present invention also includes one or more accelerators which catalyze cure

of the polymer composition, such as those described in the '330 patent. The present

invention includes an organic hydrazine. Desirably the organic hydrazine is present in

10   an amount of about 1.0% w/w or less. The organic hydrazine may be represented

generally by the following formula:

$$R^2\!-\!N\!-\!N\!-\!\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\!-\!R^3$$
$$\quad\;\;|\quad|$$
$$\quad\;\;H\quad H$$
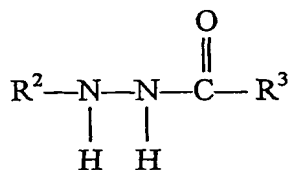
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where R^2 may be selected from the following radicals: alkyl, preferably lower alkyl

containing 1-6 carbon atoms, either straight chain or branched, more preferably methyl,

ethyl or isopropyl; cycloalkyl containing up to about 8 carbon atoms; alkenyl containing

20   up to about 10, preferably 2-5 carbon atoms, cycloalkenyl containing up to 10, preferably

up to about 6, carbon atoms; aryl, including haloalkoxy groups containing one to about 6

carbon atoms. R^3 may be hydrogen or any one of the radicals specified for R^2 and in

addition may be an amino or substituted amino group, or a carbonyl group to which is

connected an unreactive group such as a lower alkyl containing from one to about 4

25   carbon atoms. R^3 may also be either of the following groups:

$$-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{N}-R^2 \qquad \text{and} \qquad -R^{10}-\underset{\|}{\overset{O}{C}}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{N}-R^2$$

where R^{10} is selected from the group consisting of alkyl groups containing one to about

10 carbon atoms, alkenyl groups containing two to about ten carbon atoms, and aryl

groups containing up to about 10 carbon atoms. The accelerator(s) should be present in

an amount sufficient to accelerate the polymerization at room temperature.

The organic hydrazine used in the present invention is desirably an acetylphenyl

hydrazine (APH). Representative compounds according to the above general formula

which are useful in the present invention include, but are not limited to, 1-acetyl-2-

phenyl hydrazine, 1-acetyl-2(p-tolyl)hydrazine, 1-benzoyl-2-phenyl hydrazine, 1-

(1',1',1'-trifluoro)acetyl-2-phenyl hydrazine, 1,5-diphenylcarbohydrazide, 1-formyl-2-

phenyl hydrazine, 1-acetyl-2-(p-bromophenyl)hydrazine, 1-acetyl-2-(p-

nitrophenyl)hydrazine, 1-acetyl-2-(p-methoxyphenyl)hydrazine, 1-acetyl-2-(2'-

phenylethyl)hydrazine, 1-acetyl-2-methyl hydrazine, 1-phenylsemicarbazide, 2-phenyl-t-

butylcarbazate, and succinic acid di(phenylhydrazide).

Other accelerators which may be used in the present invention include, but are

not limited to, tertiary alkyl amines, rhodamine, alkoxy amines, and ferrocene

compounds.

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The present invention also includes an onium compound. It is believed that this

onium compound serves as a reducing agent. Examples of suitable onium compounds

include, but are not limited to, phosphonium and ammonium compounds, such as those

described in the '998 patent, incorporated herein by reference.

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Ammonium salts useful in the present invention may be represented by the

following formula:

$$
\begin{array}{c}
R^8 \\
| \\
R^7\!-\!N^{\oplus}\!-\!R^9 \quad X^- \\
| \\
R^{11}
\end{array}
$$

15   wherein R^7, R^8, R^9 and R^{11}, which may be the same or different, are hydrocarbyl,

hydrocarbylaryl, aryl or a substituted derivative thereof; X is Cl, Br or F or a soft anion,

such as —SbF_6, —BF_4 or PF_6.

Desirably, the onium salt is a phosphonium salt, which may be represented by the

20   following formula:

$$
\begin{array}{c}
R^{13} \\
| \\
R^{12}\!-\!P^{\oplus}\!-\!R^{14} \quad X^- \\
| \\
R^{15}
\end{array}
$$
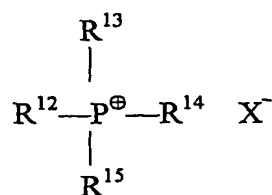
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wherein R^{12}, R^{13}, R^{14} and R^{15} which may be the same or different, are hydrocarbyl,

hydrocarbylaryl, aryl or a substituted derivative thereof; X is Cl, Br, I or F or a soft

anion, such as —SbF_6, —BF_4 or PF_6. Desirably, R^2, R^3 and R^4 are each phenyl or C_1-C_5

alkyl.

5

Desirably, the phosphonium salt used in the present invention is selected from

allyltriphenylphosphonium bromide (ATPB), 2-(ethoxycarbonyl)ethyl-

triphenylphosphonium bromide, 1-ethoxycarbonylethyl triphenylphosphonium bromide,

4-ethoxycarbonylbutyl triphenylphosphonium bromide, carbethoxymethyl

10   triphenylphosphonium bromide, or methyltriphenylphosphonium bromide.

In one aspect of the present invention, mixtures of onium salts may be used, such

as mixtures comprising combinations of different phosphonium salts, combinations of

different ammonium salts and combinations of phosphonium and ammonium salts.

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The present invention may optionally include additional ingredients, including

but not limited to saccharin, dimethyl p-toluidine (DMPT), phenolic stabilizers, and

chelating agents, may serve to modify the uncured and cured adhesive properties of the

composition.

20

It has also been discovered, however, that the present inventive compositions can

achieve their enhanced cure speed and completeness of cure in the absence of commonly

incorporated accelerators such as sulfimides, e.g. saccharin.

Having set forth examples of suitable compounds which may be present in

compositions of the present invention, specific examples of compositions which were

formulated and tested will now be set forth in detail below.

Table I

Screening Agents

Nine quaternary phosphonium and ammonium salts were used in determining

their importance in promoting cure of anaerobic adhesives in contact with magnesium

oxide. Salt 1 was synthesized as indicated below. Salts 2-9 were obtained from

commercial sources. The structures of these compounds are as follows:

Onium Salt	R
1	$-CH_2CH_2COOEt$
2	$-CH_3$
3	$-CH_2CH=CH_2$
4	$-CH(CH_3)COOEt$
5	$-(CH_2)_4COOEt$
6	$-CH_2COOEt$
7	$\begin{array}{c} Bu \\ | \\ Bu-P\oplus-Bu \quad Br^- \\ | \\ Bu \end{array}$
8	$\begin{array}{c} Bu \\ | \\ Bu-N\oplus-Bu \quad Br^- \\ | \\ Bu \end{array}$
9	$\begin{array}{c} C_8H_{17} \\ | \\ C_8H_{17}-N\oplus-CH_3 \quad Cl^- \\ | \\ C_8H_{17} \end{array}$

$Ph_3P^{\oplus}-R \quad Br^-$
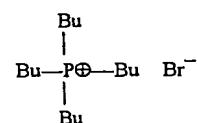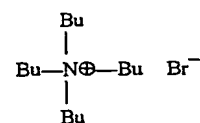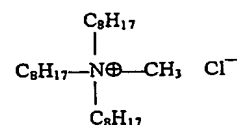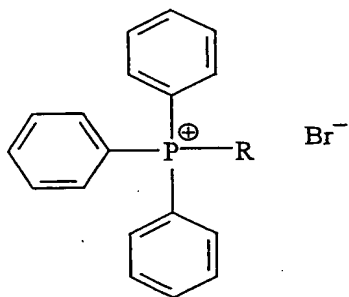
Synthesis of 2-(ethoxycarbonyl) ethyl triphenylphosphonium bromide (Salt 1):

Ethyl 3-bromopropionate (1.81g, 0.01 moles) was added to a three-necked, 100

mL round bottom flask equipped with a magnetic stirrer, thermocouple and temperature

5   controller, condenser, and heating mantle. Triphenylphosphine (2.62g, 0.01 moles) and

toluene (25 ml) was added and the mixture was heated to reflux temperature. As the

temperature turned 90°C, the mixture turned slightly cloudy. After 3 hours at 115°C, the

reaction mixture was cooled to room temperature, during which time a yellow colored

waxy material settled to the bottom of the reaction flask. The liquid was removed and

10   the residual waxy solid dissolved in dichloromethane (about 10 ml). Diethyl ether (about

15 ml) was added to the dichloromethane solution and a precipitate was formed. The

precipitate was collected by filtration and dried under vacuum to give the required

phosphonium salt (0.8 grams; 18 % yield). The structure of the product was confirmed

by ^{1}H NMR analysis.

15

Example 1

Comparison of anaerobic adhesives with and without organic hydrazine

Anaerobic adhesive Composition A was prepared from a mixture of 93.00% w/w

20   methacrylate ester monomers (78.00% urethane-methacrylate-acrylate monomers;

15.00% hydroxypropyl methacrylate), 6.00% acrylic acid, and 1.00% CHP. Five

compositions were subsequently prepared from Composition A as indicated below:

25

Table 2

Composition	Additive to Composition A	% Additive (%w/w)	Polymer	Adhesion
1	None	—	soft + tacky	poor
2	Onium Salt 1	1.0	hard + dry	poor
3	Onium Salt 3	1.0	hard + dry	poor
4	Onium Salt 9	1.0	hard + dry	poor
5	1-acetyl-2-phenylhydrazine	0.95	hard + dry	good

Cast magnesium lap-shear joints were assembled with Compositions 1-5. The

5   bondline gap was set at 0.254 mm (10 mil) and the joints were allowed to cure at room

temperature for 24 hours. After curing, a qualitative assessment of the degree of

polymerization and adhesive strength was made. All but Composition 5 showing poor

adhesion.

10   Composition 1, without added onium salt, served as a control to determine the

importance of the onium salt alone, and Composition 5, which did not include an onium

salt but did include an organic hydrazine, served as a control to determine the importance

of the organic hydrazine alone.

15   As seen in Table 2, all of the adhesive joints assembled using Compositions 1-4

showed poor adhesion by comparison to Composition 5. However, Compositions 2-4,

which contained onium salts, were found to have cured to a desirable hard and dry

polymer film, whereas Composition 1, without onium salt, was soft and tacky. This

indicates that the inclusion of onium salts and organic hydrazines to anaerobic adhesives are important in the development of cured polymer and adhesive strength on magnesium surfaces. The use of onium salts promote cure of the polymer, while the use of hydrazines promotes cure of the polymer as well as adhesive strength.

5

Example 2

To determine which onium salts are most effective at promoting adhesive strength of anaerobic adhesives on magnesium surfaces, anaerobic adhesive Composition

10   B was formulated to which onium salts 1-9 (Table I) were added. Composition B comprised a mixture of triethyleneglycol dimethacrylate (TRIEGMA) 87.5% w/w, hydroxypropyl methacrylate (HPMA) 10.0% w/w, CHP 1.5% w/w, and 1.0% w/w of the onium salt being tested. Additionally, one mixture was formulated as a control in which no onium salt was present.

15

One gram of each of the ten compositions was placed in each of two glass vials. To one vial was added 0.01 grams of magnesium shavings, which were used as a model for the alloy substrates. The vials were left at room temperature for 24 hours and then examined for gellation. The results are presented in Table 3.

20

Table 3

Results of the room temperature gel-test experiments in model anaerobic adhesives with and without magnesium turnings

Salt # Present In Composition B	Type of Salt	24 hour gel With Mg	24 hour gel Without Mg
none (control)	—	no	no
1	$P^{\oplus}$	yes	no
2	$P^{\oplus}$	yes	no
3	$P^{\oplus}$	yes	no
4	$P^{\oplus}$	no	no
5	$P^{\oplus}$	no	no
6	$P^{\oplus}$	no	no
7	$P^{\oplus}$	no	no
8	$N^{\oplus}$	no	no
9	$N^{\oplus}$	yes	yes

Compositions which gelled in the presence of magnesium turnings are sensitive to magnesium as they are activated with regard to curing in the presence of magnesium. For the purposes of the present invention, it is desired that such compositions do not gel in the absence of magnesium, in order to maintain their stability. As such, compositions containing phosphonium salts 1-3, which were found to have gelled in the presence of magnesium but not in the absence of magnesium, are ideally suited for use in the present invention. The differential reactivity of these compositions may be used to screen potentially useful compounds or activators for use in anaerobic adhesives for bonding magnesium alloys.

It has been further determined that it is important to have present, in addition to the onium salts, an organic hydrazine in order to achieve the cure speed, cure completeness and ultimate desired cure strength on passive substrates such as magnesium alloys. For example, compositions containing phosphonium salts 4-7 and the

24

composition containing quaternary ammonium salt 8, all of which did not include the

organic hydrazine, showed no reactivity towards magnesium. The composition

containing quaternary ammonium salt 9, which also did not include an organic

hydrazine, resulted in the gellation of the adhesive composition in both the presence and

5   absence of magnesium. Although this composition cures in the presence of magnesium,

it shows no differential reactivity or selectivity in the absence of magnesium, as the

compositions containing phosphonium salts 4-7 do. It should be noted that in a

screening test such as this, gellation is not necessarily an accurate measure of the ability

to obtain sufficient cure to achieve the desired adhesive. However, such screening is

10   indicative of whether there is reactivity of the composition in the presence of the passive

substrate.

These tests were repeated for compositions including onium salts 1-3 but without

added CHP in the formulation. All three compositions failed to gel within a 24 hour

15   period, indicating that both hydroperoxide and phosphonium salt are required to provide

magnesium-sensitive compositions. Taken together with Example 1, these experiments

indicate that a formulation including hydroperoxide, phosphonium salt, and an organic

hydrazine in combination with one or more monomers would be well suited for use as an

adhesive and bonding material for magnesium and related passive substrates. As such,

20   further experimentation was conducted using such inventive formulations, as indicated

below.

25

Example 3

Composition 5 (mixture of urethane-acrylate monomers, hydroxypropyl methacrylate, acrylic acid, CHP, and 1-acetyl-2-phenylhydrazine) was used as a base

5   formulation for measuring the effect of allyltriphenylphosphonium bromide (ATPB) (Salt 3 in Table I) as a curing activator on magnesium alloy substrates. Adhesive formulations containing 0.25, 0.5, 1.0, and 2.0% w/w ATPB dissolved in Composition 5 were prepared in low density polyethylene bottles by adding approximately half the required amount of Composition 5 to the bottle followed by the phosphonium salt and

10   the remainder of Composition 5.

The mixture was stirred mechanically for about thirty minutes and allowed to sit overnight at room temperature to ensure complete removal of air bubbles. Stability was performed at 82°C in 10 × 75 mm glass vials in a temperature controlled heating block

15   fitted with a calibrated thermocouple. The magnesium alloy lap-shear specimens were wiped with acetone and allowed to dry before use.

Lap-shear testing was performed on an Instron tension tester, fitted with a 1 or 5 KN load cell, at a strain of 12.7 mm/min, according to American Standard Test Method

20   (ASTM) D-1002. The tests were performed at "zero" and 0.254 mm (10 mils) gaps. A short steel U-shaped wire spacer was used to set the gap. An average of 5 measurements was made for each test. The adhesive strength was determined as a function of the curing times under ambient conditions. For comparative purposes, Composition 5 was evaluated as a control formulation. The results obtained at "zero" gap are presented in

Table 4 and Figures 1 and 2 below and the results obtained at 0.254 mm gap are

presented in Table 5 and Figure 3 below.

Table 4

5   **Lap-shear test results of onium salt-modified anaerobic adhesive on magnesium**

alloy substrates at "zero" gap (average 5 specimens)

Curing Time (hours)	Composition 5 (MPa)	Composition 5 + 0.25% ATPB (MPa)	Composition 5 + 0.5% ATPB (MPa)
2	0.7 ± 0.3	5.8 ± 1.0	6.8 ± 1.7
4	3.4 ± 1.9	6.9 ± 2.0	7.4 ± 3.3
24	5.2 ± 0.9	—	6.7 ± 2.7

10

Figures 1 and 2 illustrate diagrammatically the results shown in Table 4. As seen

in Figure 1, at "zero" gap, the composition containing 0.25% ATPB shows an eight-fold

increase of curing rate compared to the control Composition 5. Additionally, the

15   ultimate strength obtained is enhanced by the presence of the phosphonium salt. As seen

in Figure 2, similar results were obtained for the composition containing 0.5% ATPB. In

this case, the curing rate of the onium modified composition is ten times that of the

control Composition 5 without added salt. In this figure, it is clear that the ultimate

strength of the modified composition is obtained in less than two hours, whereas the

20   unmodified control Composition 5 has not reached this value even after 24 hours.

Example 4

ATPB was also found to accelerate the curing of Composition 5 (Control) at the

relatively large bondline gap of 0.254 mm (10 mil), as shown in Table 5 and Figure 3.

25

Table 5

Lap-shear test results of onium salt-modified anaerobic adhesive on magnesium

alloy substrates at 0.254 mm (10 mil) gap (average 5 specimens)

5

Curing Time (hours)	Composition 5 (MPa)	Composition 5 + 0.25% ATPB (MPa)	Composition 5 + 0.5% ATPB (MPa)	Composition 5 + 1.0% ATPB (MPa)	Composition 5 · 2.0% ATPB (MF
2	0.1 ± 0.1			5.4 ± 2.0	
4			6.1 ± 2.1	8.0 ± 2.7	
8	0.6 ± 0.4		9.1 ± 3.7	3.0 ± 0.7	4.9 ± 1.3
24	1.4 ± 0.4	7.0 ± 1.4	5.0 ± 1.2		
72	2.5 ± 0.3		7.2 ± 0.9	4.0 ± 1.0	
168	2.9 ± 0.4		8.1 ± 2.9		

10   As seen in Table 5, at a level of approximately 1.0% w/w ATPB, the cure speed

is enhanced by a factor of approximately 50 and the ultimate strength is achieved within

the first four hours of curing. In contrast, the unmodified adhesive Composition 5 cures

only very sluggishly and never reaches more than 1/3 the ultimate strength. As seen in

Figure 3, at a level of approximately 0.5% w/w ATPB, ultimate cure was achieved

15   within the first eight hours of curing and was enhanced by a factor of approximately 15.

These results clearly demonstrate the ability of the present inventive compositions to

cure through large gaps.

Example 5

20

        Desirably, base Composition 5 is stable for at least two hours at 82°C. The

addition of one percent of the phosphonium salt ATPB was observed to decrease the

stability of Composition 5 at this temperature. However, reducing the amount of salt

resulted in a product which exhibited stability similar to that of Composition 5 alone

25   while maintaining the desirable adhesive characteristics of the modified Composition 5.

Stability tests were conducted on base Composition 5 mixed with various amounts of

ATPB and maintained at 82°C, as shown in Table 6. All of the formulations showed

good stability on ambient storage over a six-week period.

5

Table 6

82°C Stability of Composition 5 with added ATPB

Amount of added ATPB (% w/w)	Gel Time (hours)
None	>2
1	0.5-0.75
0.5	1.0-1.25
0.25	>2

10

Example 6

Anaerobic adhesive Compositions 6-8 were prepared by blending together the

ingredients listed in Table 7. The resin mixtures comprised a blend of urethane acrylate

15   prepolymers, monomers, and polymerization stabilizers typically used in the formulation

of anaerobic adhesives.

Table 7

Formulations of anaerobic adhesive compositions 6-8. All amounts are expressed in

20   % by weight

Component	Composition 6	Composition 7	Composition 8
Resin Mixture	97.25	97.75	97.75
CHP	1.00	1.00	1.00
ATPB	0.75	0.75	0.75
APH	1.00	0.50	
Saccharin			0.50

25

The liquid compositions were used to assemble magnesium alloy lap-shear specimens having an induced gap of 0.254 mm (10 mil). The assembled specimens were allowed to cure at room temperature for 5.5 hours and tested according to the ASTM procedure set forth above. The results are presented in Table 8.

5

Table 8.

Lap-shear adhesive strength test results for adhesive compositions 6-8 on magnesium substrates. Values are the average of 5 measurements.

10

Adhesive	Stress at break (MPa)	Mode of Failure
6	5.7	adhesive
7	5.3	adhesive
8	1.1	cohesive

As seen in Table 8, the inventive compositions containing APH have significantly enhanced performance on magnesium compared with the same composition

15   containing saccharin. On average, the APH containing formulations (Compositions 6 and 7) exhibit five times the adhesive strength of the comparable material containing saccharin (Composition 8). The results also demonstrate that concentrations of APH lower than 1% are effective in activating the onium salt containing anaerobic adhesives on magnesium substrates as no significant different in the adhesive strengths of

20   Compositions 6 and 7 are seen, yet Composition 7 contains only half the amount of APH that is present in Composition 6.

An examination of the substrates following the adhesive tests showed that Compositions 6 and 7 were hard and well cured, whereas Composition 8 was soft, tacky,

and only partially cured. These differences in the degree of curing are reflected in the observed modes of failure.

Example 7

5

To further study the effects of APH in the present invention, anaerobic adhesive Compositions 9 and 10 were prepared by blending together the ingredients listed in Table 9.

10

Table 9.

Formulations of anaerobic adhesive compositions 9 and 10. All amounts are expressed in % by weight.

Component	Composition 9	Composition 10
Resin Mixture	96.65	96.65
CHP	1.89	1.89
ATPB	0.50	0.50
APH	0.96	
Saccharin		0.96

15

Lap-shear tests where performed on magnesium substrates as described in the above examples following a 4-hour room temperature cure. The results are presented in Table 10.

20

25

Table 10.

Lap-shear adhesive strength test results for adhesive compositions 9 and 10

(average 5 measurements)

Adhesive	Stress at break (MPa)	Mode of Failure
Composition 9	4.2	adhesive
Composition 10	0.3	cohesive

As seen in Table 10, the adhesive strength of Composition 9, containing APH, is 14 times that of the same composition containing a similar level of saccharin. The results confirm the superiority of APH over saccharin in promoting cure and adhesion of onium salts-containing anaerobic adhesives on magnesium substrates. The small reduction in adhesive strength of Composition 9 compared to Compositions 6 and 7 is likely due in part to the lower concentration of onium salts and in part to the shorter curing time of Composition 9 compared to Compositions 6 and 7.

Example 8

A determination of the curing rates of anaerobic adhesives on magnesium alloy substrates

A kinetic study on the room temperature (RT) curing of phosphonium salt-containing anaerobic adhesives was carried out by infrared spectroscopic analysis in attenuated total reflectance mode (ATR). In these experiments, a thin film of the liquid adhesive was sandwiched between a release treated zinc selenide (ZnSe) ATR crystal and a panel of AZ91D magnesium alloy, machined to the same dimensions of the crystal. The progress of anaerobic curing was then monitored in real-time by following the disappearances of absorbance bands associated with the reactive double bond of the

(meth)acrylate groups at 1637 cm^{-1}. Curing is initiated as soon as the substrate is applied

to the liquid adhesive film and air is excluded from the joint. The method permits an

accurate measure of the rate and extent of curing in an adhesive bondline that is in direct

contact with the metal substrate employed. The fractional conversion of monomer was

5   determined from the normalized ratio of the (meth)acrylate group absorbance at 1637

cm^{-1} to the carbonyl group absorbance at 1710 cm^{-1} according to the expression 1-R_t/R_0,

where R_0 is the initial ratio (i.e. at time = 0) and R_t is the corresponding ratio at some

time during or after the curing reaction (i.e. at time = t).

10   For the purposes of evaluating the effect of onium salts on the curing reactivity of

anaerobic adhesives a test composition was prepared by blending together the

components detailed in Table 11.

Table 11

15   **Anaerobic adhesive test composition used in IR curing studies.**

Component	Weight %
urethane methacrylate (UM) resins	76.14
2-hydroxypropyl methacrylate	14.80
acrylic acid	6.20
cumene hydroperoxide	1.90
2-acetylphenylhydrazine	0.95
stabilizers	0.01

The curing of this composition without onium salt was analyzed by the method

described above, which showed that after about 400 minutes from the time of assembly,

the extent of curing had only reached a value of about 40% as shown in Figure 4.

20   However, the addition of 0.5% of methyltriphenylphosphonium bromide to the test

composition had a significant accelerating effect on the rate of curing and resulted in

33

higher degree of curing (~80%) compared to the formulation without the onium salt

catalyst (Figure 4). After 3 hours, the curing of the composition with added MTPB is

almost complete (~80% conversion), whereas the unmodified product has only reached

~35% conversion in the same time. It can also be seen from the conversion plots in

5   Figure 4 that, in the presence of MTPB, the initial curing rate is considerably more rapid

compared to the composition without catalyst and that the small induction time or

inhibition is not observed. After a conversion of about 70% of the (meth)acrylate groups

the curing rate decreases sharply. This is most likely the result of gellation and

vitrification. Curing was performed on ZN Se/AZ91D magnesium alloy bondline.

10

Analysis of the above data shows that the initial curing period (0-65 minutes) can

be conveniently described in terms of a first-order reaction where conversion rate is

directly proportional to monomer concentration. Thus rate constants for monomer

consumption during this period can be determined from the slopes of plots of $\ln[M]/[M_0]$

15   as a function of curing time. The ratio $[M]/[M_0]$ is the normalized concentration of

methacrylate groups at any time during cure as determined by IR analysis. The results

are shown in Figure 5. Figure 5 is a first-order plot for initial monomer conversion on

magnesium alloy AZ91D during room temperature cure. The corresponding rate

constants for the compositions with and without MTPB are $15.4(10^{-3})$ and $3.2(10^{-3})$/min.

20   respectively. Thus, at a level of 0.5%, MTPB accelerates the initial curing speed of the

test anaerobic adhesive on magnesium alloy by a factor of about 5 times.

The same technique was used to determine the optimum levels of APH and

MTPB in the above formulation. At a constant concentration of APH the optimum level

25   of MTPB was found to be between 0.1 and 0.5% by weight. In a related set of

34

experiments the APH levels were varied between 0.25 and 2.0% at a constant

concentration of 0.25% MTPB. These data show that APH levels in excess of 1.5 % by

weight have no additional affect on the cure speed.

5

Example 9

Anaerobic adhesive composition containing tetrabutylammonium bromide

10

A modified anaerobic adhesive composition was prepared by blending together

2.5 g of a 10% solution of tetrabutylammonium bromide (TBAB) in 2-hydroxypropyl

methacrylate and 97.5 g of the anaerobic adhesive formulation described in Table 11.

This provided an adhesive composition containing 0.25% by weight of onium salt. Lap-

15 shear adhesive testing was conducted on magnesium alloy substrates at 0.254 mm gap as

described in Example 3. The specimens were cured at room temperature for 4 hours.

For comparative purposes the adhesive without added salt was also evaluated. The

results are presented in Table 12.

20   Table 12

**Lap-shear test results of anaerobic adhesives with and without TBAB on Mg alloy
specimens after curing at RT (0.254 mm gap; average of 5).**

Composition	Curing time (hours)	Average lap-shear strength (MPa)	Coefficient of variation (%)
With 0.25% TBAB	4	6.0	13
Without TBAB	8	0.6	67

25

After curing for 4 hours at RT, the composition without added catalyst was so

weakly bonded that the specimens broke before the test could be completed. The curing

of this sample was, therefore, extended to 8 hours to enable the lap-shear strength to be

30 measured. The large variance in the data as indicated by the coefficient of variation for

the composition without TBAB further demonstrates that there is a lot of variation in the

degree of curing from one specimen to the others. These results in conjunction with the

results of Example 2, demonstrate that the addition of TBAB to anaerobic adhesives

containing APH, activates the adhesive to curing on magnesium alloy substrates.

5

Example 10

**An evaluation of the catalyst modified anaerobic adhesives on various passive
substrates**

10

An anaerobic adhesive was prepared by dissolving 0.25% by weight

allyltriphenylphosphonium bromide (ATPB) into the test adhesive of Example 8. Lap-

shear adhesive strength tests were performed on various substrates, which are known to

15   be passivating towards the curing of anaerobic adhesives. The values were then

compared to the unmodified adhesive (control sample) cured under the same conditions

(cured at RT for 24 hours, 0.254 mm gap, average 5 specimens). In all cases, the ATPB-

modified adhesive gave higher strengths compared to the unmodified material. The

results are summarized in Table 13. The sensitivity of an adhesive to the various

20   substrate surfaces is measured from the ratio of adhesive strength values of the

compositions with and without added onium salt catalyst (A/C).

25

30

Table 13

Lap-shear adhesive test results ATPB modified and unmodified anaerobic adhesives on various passive substrates (RT 24h; 0.254 mm; 5 specimens)

Substrate	ATPB (A) (MPa)	Control (C) (MPa)	Surface Sensitivity (A/C)
Anodized aluminum	11.2	7.1	1.6
Zinc dichromate steel	6.0	1.8	3.3
Stainless steel	8.0	5.0	1.6
Magnesium	7.0	1.4	5.0

Although the activity of the anaerobic adhesive modified with the onium salt is enhanced on all the substrates examined, the proportional increase in strength (A/C ratio) is greatest for magnesium, indicating a high surface sensitivity towards this substrate. By comparison, the surface sensitivities (A/C) to anodized aluminum and stainless steel are relatively low. With zinc dichromate the value was intermediate, suggesting that onium salt containing compositions may also be useful for the bonding of these substrates.

In the inventive compositions containing ATPB, the percentage increase in adhesive strength on magnesium is 400% greater than the control; on stainless steel is a 60% increase over the control; zinc dichromate steel is 233% increase over the control; and on amodized aluminum is 58% greater than the control.

Example 11

Anaerobic sealant compositions

The usefulness of onium salts for promoting the curing of anaerobic sealant compositions on magnesium substrates was also demonstrated. A composition having

good sealing properties was prepared by blending together the components shown in

Table 14.

Table 14

Anaerobic Sealant Composition

Component	Weight %
polyether-urethane methacrylate (PUM) resins	82.00
2-hydroxypropyl methacrylate	2.50
acrylic acid	4.00
silica	8.50
cumene hydroperoxide	2.00
2-acetylphenylhydrazine	0.99
stabilizers	0.01

A similar composition containing additionally 0.25% allyltriphenylphosphonium

bromide (ATPB) was also prepared. The lap-shear adhesive strength development of the

two compositions was then compared on AZ91D magnesium alloy specimens (as

described in Example 3). The results are presented in Table 15.

Table 15
Adhesive test results of anaerobic sealant composition on AZ91D magnesium alloy (cured 24h at RT; 0.254 mm gap; 5 specimens)

Formulation	Average lap-shear strength (MPa)	Coefficient of variation (%)
With 0.25% ATPB	2.9	24
Without catalyst	0.9	11

The results indicate that there is an approximate 3-fold increase in adhesive

strength for the sealant composition containing ATPB compared to the same sealant

composition without the catalyst. The catalyst thus promotes the curing and adhesive

strength development of the anaerobic sealant composition on magnesium substrates.

The examples set forth above serve to illustrate the present invention, but in no way are intended to limit the spirit and scope thereof, which is defined by the following claims.
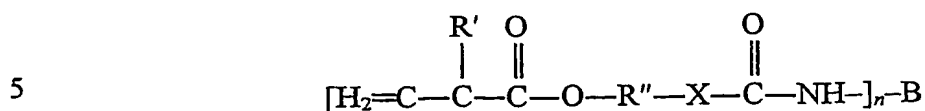
WHAT IS CLAIMED IS:

1.   A one-part adhesive composition which provides enhanced bonding on passivated substrates, comprising: (a) at least one monomer; (b) at least one peroxy free radical initiator; (c) at least one onium salt; and (d) at least one organic hydrazine.

2.   The composition of claim 1, wherein said monomer is anaerobically curable.

3.   The composition of claim 1, wherein said monomer is curable by a moisture cure mechanism, heat cure mechanism, photo initiator mechanism and combinations thereof.

4.   The composition of claim 1, wherein said monomer is an (meth)acrylate monomer.

5.   The composition of claim 1, wherein said monomer is selected from the group consisting of styrene, thiol-enes, acrylamides, maleate esters, fumarates, methylene maleates, and epoxides.

6.   The composition of claim 4, wherein said (meth)acrylate monomer is selected from the group consisting of diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 5   diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, polyethylene glycol diacrylate, di(pentamethylene glycol) dimethacrylate, tetraethylene

glycol di(chloroacrylate), diglycerol diacrylate, diglycerol tetramethacrylate, butylene

glycol dimethacrylate, neopentyl glycol diacrylate, trimethylolpropane triacrylate,

hydroxypropyl methacrylate and combinations thereof.

7.   The composition of claim 4, wherein said (meth)acrylate monomer is

selected from the group consisting of ethoxylated trimethylolpropane triacrylate,

trimethylol propane trimethacrylate, dipentaerythritol monohydroxypentacrylate,

5   pentaerythritol triacrylate, ethoxylated trimethylolpropane triacrylate, 1,6-

hexanedioldiacrylate, neopentyl glycoldiacrylate, pentaerythritol tetraacrylate, 1,2-

butylene glycoldiacrylate, trimethylopropane ethoxylate tri(meth)acrylate, glyceryl

propoxylate tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, dipentaerythritol

monohydroxy penta(meth)acrylate, tri(propylene glycol) di(meth)acrylate,

10   neopentylglycol propoxylate di(meth)acrylate, 1,4-butanediol di(meth)acrylate,

polyethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, butylene glycol

di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate and combinations thereof.

8.   The composition of claim 4, wherein said (meth)acrylate monomer is a

polyurethane (meth)acrylate monomer.

9.   The composition of claim 8, wherein said polyurethane (meth)acrylate

monomer has the structure:

$$[H_2{=}C{-}\overset{\displaystyle R'}{\underset{\displaystyle |}{C}}{-}\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}{-}O{-}R''{-}X{-}\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}{-}NH{-}]_n{-}B$$

5

wherein B is a polyvalent organic radical selected from the group consisting of alkyl,

alkenyl, cycloalkyl, aryl, aralkyl, alkaryl and heterocyclic radicals both substituted and

10   unsubstituted; X is selected from the group consisting of —O— and

$$\begin{array}{c} R \\ | \\ \text{—N—} \end{array}$$

15

radicals; n is an integer from 2 to 6 inclusive; R' is selected from the class consisting of

hydrogen, chlorine and methyl and ethyl radicals; and R" is a divalent organic radical

selected from the group consisting of lower alkylene of 1 to 8 carbon atoms, phenylene

and naphthalene radicals.

10.   The composition of claim 1, wherein said peroxy free radical initiator is

cumene hydroperoxide.

11.   The composition of claim 1, wherein said peroxy free radical initiator is

selected from the group consisting of methylethyl ketone hydroperoxide, t-butyl

hydroperoxide, p-menthane hydroperoxide, diisopropylbenzene hydroperoxide, pinene

hydroperoxide, and combinations thereof.

12.   The composition of claim 1, wherein said onium salt is selected from the

group of the group consisting of phosphonium salts, ammonium salts, and combinations

thereof.

13.   The composition of claim 12, wherein said phosphonium salt is

represented by the structure:

$$R^1—\overset{\overset{\textstyle R^2}{\textstyle |}}{\underset{\underset{\textstyle R^4}{\textstyle |}}{P^{\oplus}}}—R^3 \quad X^-$$
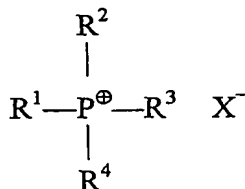
5

wherein R^1, R^2, R^3 and R^4, which may be the same or different, are hydrocarbyl,

hydrocarbylaryl, aryl or a substituted derivative thereof; X is Cl, Br or F or a soft anion,

such as —SbF_6, —BF_4 or PF_6.

14.   The composition of claim 12, wherein said phosphonium salt is selected

from the group consisting of 2-(ethoxycarbonyl) ethyl triphenylphosphonium bromide,

1-ethoxycarbonyl ethyl triphenylphosphonium bromide, 4-ethyoxycarbonylbutyl

5   triphenylphosphonium bromide, carbethoxymethyl triphenylphosphonium bromide, and

combinations thereof.

15.   The composition of claim 12, wherein said phosphonium salt is

allyltriphenylphosphonium bromide.

16.   The composition of claim 1, wherein said onium salt is present in an

amount from about 0.25 to about 2.0 % by weight of said composition.

17.   The composition of claim 1, wherein said organic hydrazine is selected

from the group consisting of 1-acetyl-2-phenyl hydrazine, 1-acetyl-2(p-tolyl)hydrazine,

1-benzoyl-2-phenyl hydrazine, 1-(1',1',1'-trifluoro)acetyl-2-phenyl hydrazine, 1,5-

5   diphenylcarbohydrazide, 1-formyl-2-phenyl hydrazine, 1-acetyl-2-(p-

bromophenyl)hydrazine, 1-acetyl-2-(p-nitrophenyl)hydrazine, 1-acetyl-2-(p-

methoxyphenyl)hydrazine, 1-acetyl-2-(2'-phenylethyl)hydrazine, 1-acetyl-2-methyl

hydrazine, 1-phenylsemicarbazide, 2-phenyl-t-butylcarbazate, succinic acid

di(phenylhydrazide), and combinations thereof.

18.   The composition of claim 1, wherein said organic hydrazine is present in

an amount of about 1.0 % or less of said composition by weight.

19.   The composition of claim 1, further comprising ingredients selected from

the group consisting of saccharin, dimethyl p-toluidine, phenolic stabilizers, chelating

agents, and combinations thereof.

20.   An anaerobic adhesive composition having improved adhesion to passive

substrates comprising: (a) at least one (meth)acrylate monomer; (b) at least one peroxy

free radical initiator; (c) at least one phosphonium salt; and (d) acetylphenyl hydrazine.

21.   A method for providing enhanced adhesion to passive substrates,

comprising the steps of:

        a)   providing a composition comprising (i) at least one monomer; (ii)

5   at least one peroxy free radical initiator; (iii) at least one onium salt; and (iv) at least one

organic hydrazine;

        b)   disposing said composition between two substrates; and

        c)   effecting cure of said composition to effectuate enhanced adhesion

thereof.

22.   A method of making an anaerobic adhesive composition having improved

adhesion to passive substrates such as magnesium, comprising the steps of:

a)   providing at least one monomer, at least one peroxy free radical

initiator, at least one onium salt; and at least one organic hydrazine; and

5   b)   combining each of said components to form a mixture.

Figure 1.

Dependence of lap-shear adhesive strength of room temperature curing time of Composition 5 with and without 0.25% ATPB; (magnesium substrates; "zero" gap)
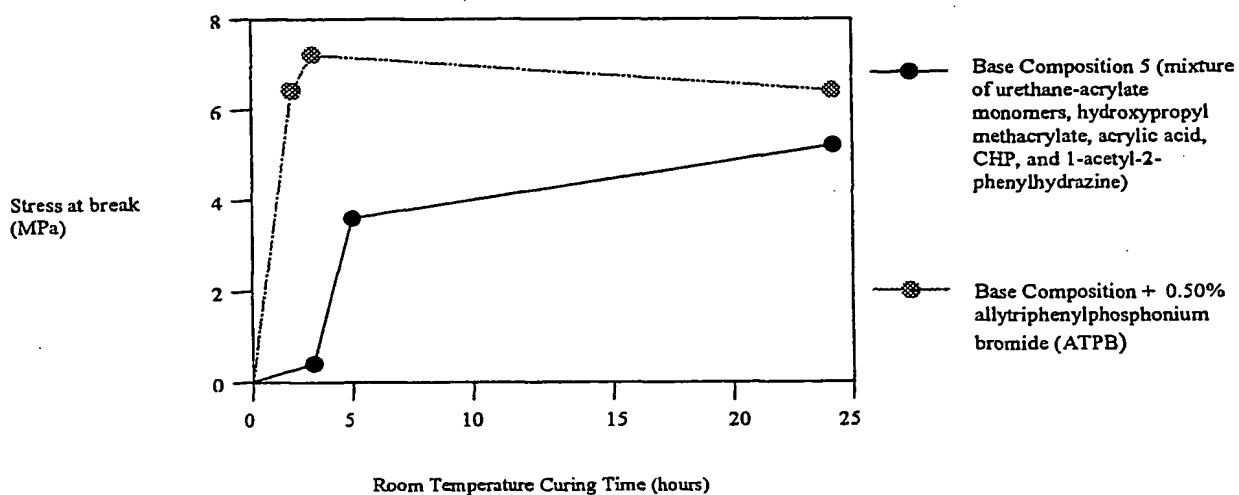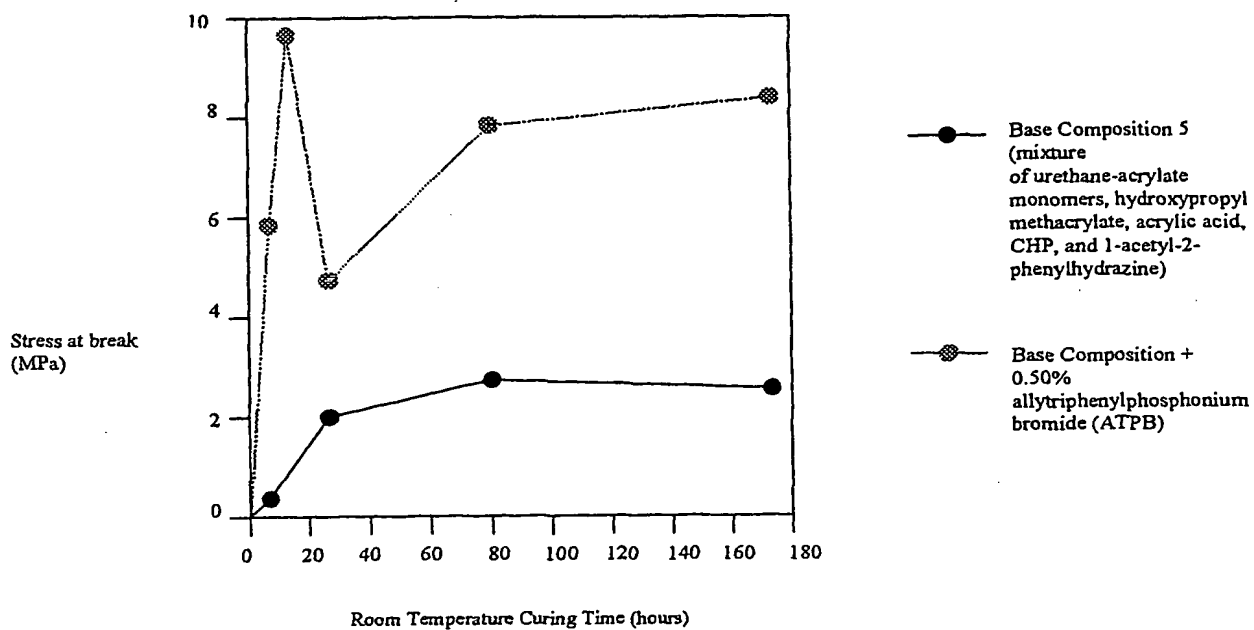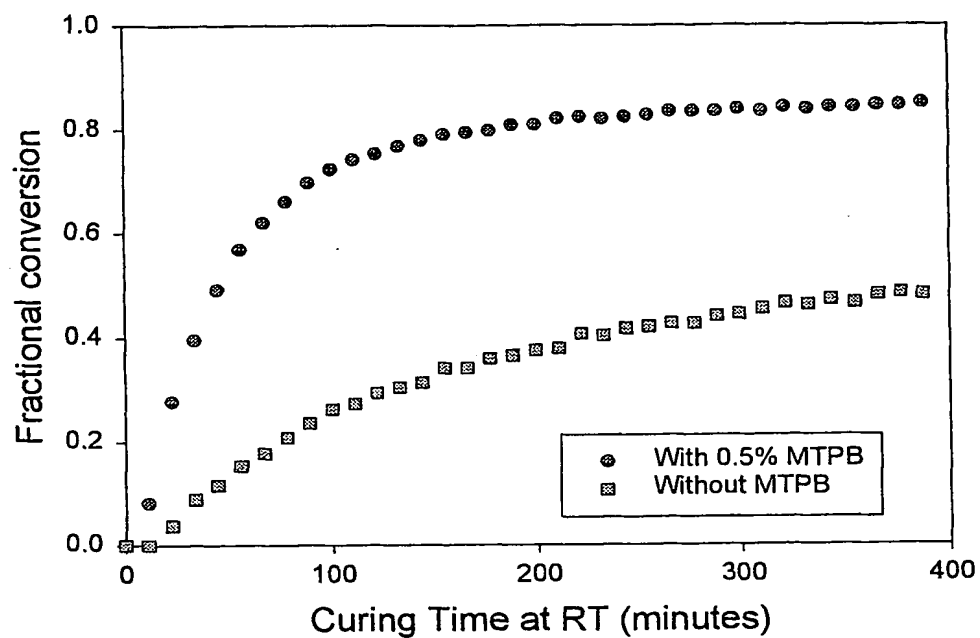

Stress at break (MPa) vs Room Temperature Curing Time (hours)

Base Composition 5 (mixture of urethane-acrylate monomers, hydroxypropyl methacrylate, acrylic acid, CHP, and 1-acetyl-2-phenylhydrazine)

Base Composition + 0.25% allytriphenylphosphonium bromide (ATPB)
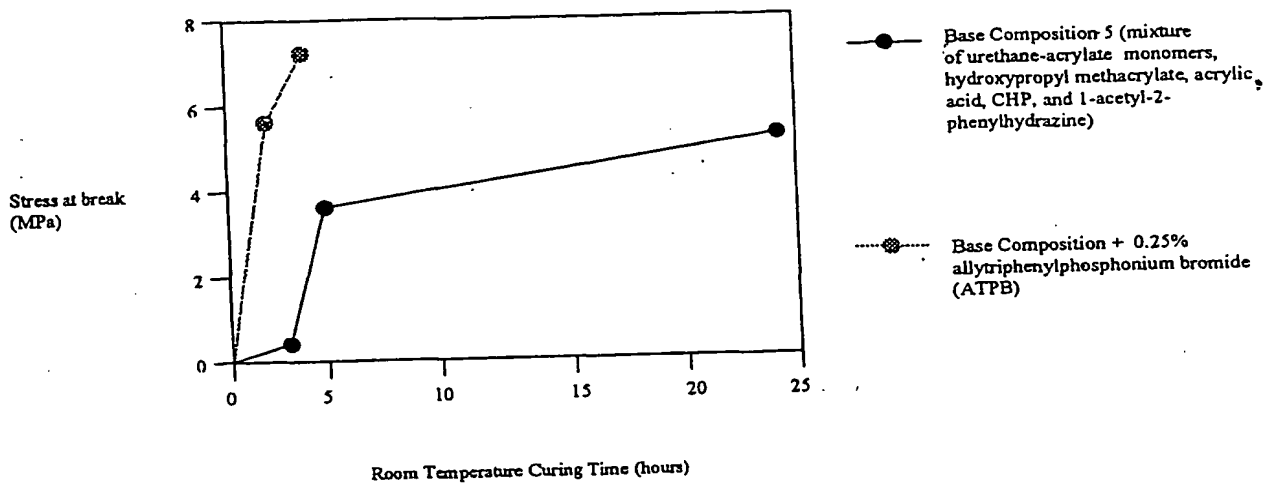
Figure 2.

Dependence of lap-shear adhesive strength on room temperature curing time of Composition 5 with and without 0.5% ATPB; (magnesium substrates; "zero" gap)

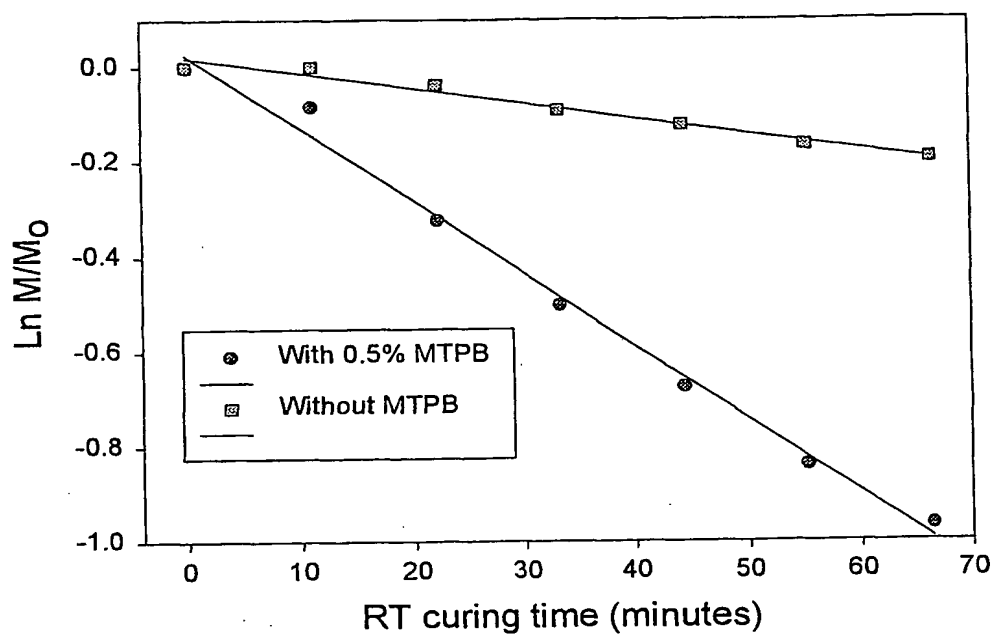Stress at break (MPa) vs. Room Temperature Curing Time (hours)

Legend:
- ●— Base Composition 5 (mixture of urethane-acrylate monomers, hydroxypropyl methacrylate, acrylic acid, CHP, and 1-acetyl-2-phenylhydrazine)
- ⊛— Base Composition + 0.50% allytriphenylphosphonium bromide (ATPB)

Figure 3
Dependence of lap-shear adhesive strength on Room Temperature curing time of Composition 5 with and without 0.5% ATPB on Magnesium substrates at 0.254 mm gap.

Stress at break (MPa)

Room Temperature Curing Time (hours)

● ——— Base Composition 5 (mixture of urethane-acrylate monomers, hydroxypropyl methacrylate, acrylic acid, CHP, and 1-acetyl-2-phenylhydrazine)

⬢ ——— Base Composition + 0.50% allytriphenylphosphonium bromide (ATPB)

Figure 4

Figure 5